A Hypothesis of Molecular Configuration in Three Dimensions of Space.

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

(Received April 1, 1916.)

It is now almost universally acknowledged that the valency of an element is due to its being associated with one or more electrons. The mechanism of chemical combination was sketched by me in the Presidential Address to the Chemical Society* in the sentence:—"If it be conceded that a salt differs from its solution only in so far as the mobility of the solution permits of transfer of ions, the transfer of an electron from the sodium to the chlorine must take place at the moment of combination. Symbolised, if we write E for electron and simplify the reaction, dealing for the moment with an atom and not with a molecule of chlorine, we have

$$\mathrm{ENa} + \mathrm{Cl} = \mathrm{NaECl}.$$

Here the electron serves as the bond of union between the sodium and the chlorine. . . . If it be desired to form a mental picture of what occurs, let me suggest a fanciful analogy which may serve the purpose: it is that an electron is an amœba-like structure, and that ENa may be conceived as an orange of sodium surrounded by a rind of electron; that on combination the rind separates from the orange and forms a layer or cushion between the Na and the Cl, and that on solution an electron attaches itself to the chlorine in some similar fashion, forming an ion of chlorine. It will be noticed that the E fills the place usually occupied by a bond; thus Na—Cl. It happens providentially that the bond and the negative sign are practically the same; Na—Cl may be supposed to ionise thus, Na(—Cl), the negative charge or electron remaining with the chlorine."

It is proposed in the present paper to elaborate this conception, and to attempt to show by help of models the kind of mechanism which may be concerned when two or more elements form a compound. Before proceeding further, however, in order that there shall be no misunderstanding, it should be stated that the subject of this memoir is not directly connected with what may be called the permanent constitution of the atom. There is a strong consensus of opinion that an atom consists of a congeries of electrons; it is supposed by some that there is a central positive nucleus which holds them in place; these electrons are undoubtedly in rapid motion, and it will

* 'Chem. Soc. Trans.,' 1908, p. 781.

be assumed that unless they are under disturbance from collisions, when there will be slight oscillatory deformation, they move in circular orbits. The "Zeeman effect" is due to a hastening of these orbits by magnetic influence.

We have not to do with these electrons; as a whole they constitute what may be termed the essential outworks of the atom, determining its interaction with other objects. Their positions and relationships have been studied by several investigators; to avoid laborious calculations one has used magnetised needles passing through discs of cork floating in water, another has employed electrified spheres of metal hanging from a support. These discs or spheres group themselves into a triangular form if there are three such; into the form of a square, or of a triangle with a disc or sphere in the middle, if there are four; and so on. It is suggested that these groupings imitate those of the electrons in the atom.

Apart from such constitutional electrons there appear to be attached to each atom one, two, three, four, or five—rarely six, seven, or eight—electrons more loosely connected, which determine the valency of the atom. They differ from the "constitutional" electrons in so far as they are removable without disturbing the groupings which determine the essential structure of the atom as a whole. It appears probable, however, that the constitutional electrons are also removable; in fact, there is such removal from all radioactive elements when they lose a β-corpuscle; but then these radioactive elements are fundamentally altered, they cease to conserve their qualities, and they change into other forms of matter. Whether the elements not recognised as radioactive are capable of similar transformations is not yet fully elucidated; evidence, however, has been accumulating that transformation can under favourable conditions be detected. Such fundamental changes as are occasioned by the loss of a β-particle are irreversible —*i.e.*, they occur too far removed from an equilibrium to leave any opportunity for recombination; the original matter has never yet been reconstituted by addition of a β-particle. But the changes which take place when a valency electron is lost or gained are observed to occur in quantity in the reverse direction, and reach an equilibrium; they form the familiar phenomena of the change of an atom into an ion, or *vice versâ* as opportunity offers.

For the purpose of this investigation then, in which we do not concern ourselves with the inner structure of the atom, it will be considered as a sphere. But the valency electron (if there is only one) will be supposed to revolve round that sphere. A procession of electrons in rapid circular motion functions like a current of electricity in a circular coil of wire.

Hence the system atom plus electron can be imitated by the system ball plus coil of wire carrying a current. Kammerling Onnes has recently shown that if a current be induced in a coil of lead wire at 1·7° absolute, the current persists for many hours. Here we have, through absence of electric resistance, a close imitation of what is attempted by the device to be described.

Experiment shows that when a current is passed through two parallel wires, in the same direction through each, these wires attract each other. Conversely, when a current passes in one wire in the opposite direction to that in a parallel wire, these wires repel one another. Should the current-bearing wires be not parallel to each other, they tend to come together by the attraction, which is greater where they are closer. If rigid current-bearing coils be substituted for the straight wires, then the resultant action between them is most simply expressed by saying that it produces a motion which increases for each coil the number of lines of magnetic force which thread through it in agreement with the lines of its own field.

It is convenient to describe a current through a circular coil as "clockwise" or "counter-clockwise," as viewed from some specified point. There is a complete equivalence as regards external forces between a plane coil of wire through which a current is passing—or its analogue, a stream of electrons revolving in a circular orbit—on the one hand, and a uniformly magnetised magnetic shell whose boundaries coincide with those of the coil, on the other. Thus a flat current-bearing coil and also a stream of electrons revolving in a circular orbit may be regarded as the equivalents of a thin disc-shaped magnet of which one surface is composed of north and the other of south poles. This well-known conception will be found convenient in considering the attractions and repulsions produced by currents passing through coils of wire; the one side of the coil may be termed the "north-seeking," or, more briefly, the "north" side, and the other the "south" side.

Certain assumptions will now be made on which the theory of valency will be based. First, it is supposed that the path of the electron round the atom, which is taken as spherical, is not in a great circle, but that its orbit is a smaller circle parallel to some equatorial plane fixed in the atom; it may be imagined that this path is forced on the valency electron owing to the balance of forces from the asymmetry of the more rigid distribution of constituent electrons represented here by the sphere.* The point of view from

* If the structure were symmetrical around the centre, these orbital electrons would, as in familiar theories, be distributed in rings in an equatorial plane, and are illustrated by the groupings of magnetic needles in a plane.

which the electron is defined as clockwise, or anti-clockwise, as the case may be, is the nearer pole of the orbit on the sphere.

Second, the circular orbits of different valency electrons need not necessarily have all the same diameters.

Third, it will be assumed that some electrons may, owing to necessary conditions of stability, revolve clockwise, while others may have an anti-clockwise path, relative to the nearest pole on the sphere as defined above. It will also be assumed that atoms in which the path is clockwise are what is known, from the chemical point of view, as electro-negative; such atoms as those of sodium, calcium, etc.; while, if the path of the electron round the atom is anti-clockwise, the atom belongs to the class including chlorine, oxygen, etc.—the class termed electro-positive. In fig. 1 a sketch is given of a monovalent atom of the former class; in fig. 2, of an electro-positive monovalent atom. The first figure is a front, the second a side, view.

A molecule of hydrogen consists of two atoms. How are they kept together? Each atom may be supposed to belong to the class depicted in fig. 1; both atoms possess an electron rotating clockwise. This question

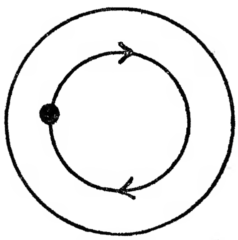

FIG. 1.

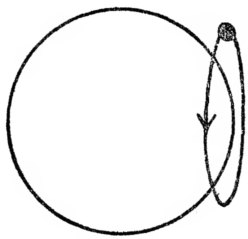

FIG. 2.

was in a sense answered by experiment. The model of the atom consisted of a "ping-pong" ball; it is a hollow sphere of celluloid, very light and fairly rigid. At each end of a diameter a brass cup was glued, and from the convex centre of each cup a fine needle projected; these were carefully centred, so that the ball rotated on them as an axis. To represent the electron, a coil of silk-covered wire was glued to the side of the ball, at right angles to its equator; one end of the wire of the coil was attached by solder to one needle and the other to the other needle. One of the needles was pivoted in a shallow glass cup, containing a liquid alloy of tin and mercury; the other passed through a perforation in a copper cup, also containing tin amalgam; it was found that in this position the ball was free to rotate with very little friction when placed with the axis vertical. The coil of wire was counterbalanced by an idle coil, so that the centre of gravity of the ball should be in the centre of the sphere. From each cup a wire was led to a switchboard

consisting of paraffin cups containing mercury which could be connected by bridge wires in any desired way, and also with the two poles of a battery. By changing the poles, the current could be taken through the wire in the clockwise or anti-clockwise direction as desired. Two such spheres were placed alongside of each other, with their axes of rotation parallel, as near each other as the position of the coils would permit. The appearance of these balls is shown in fig. 3.

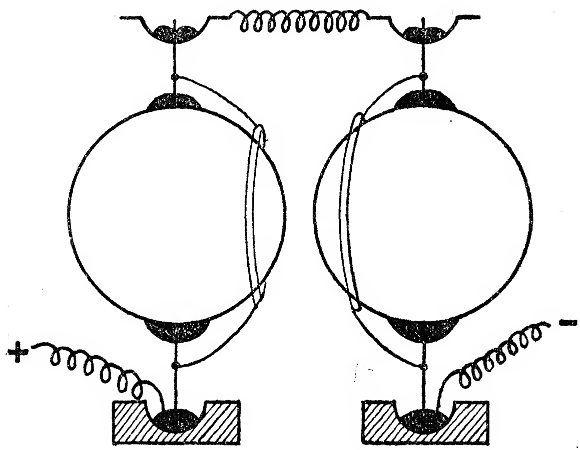

Fig. 3.

For diagrammatic purposes it is better to depict these balls with their attached coils in plan, looking vertically down on the upper needle; the coils may then be represented as chords to the circles. The direction of the current may be denoted by the letters C or AC, clockwise or anti-clockwise; the coil is to be looked at from the front.

The electrons on two atoms of hydrogen may then be imagined to be rotating clockwise; how will the balls place themselves as regards each other? This is shown in fig. 4; it is the stable position. There is also a

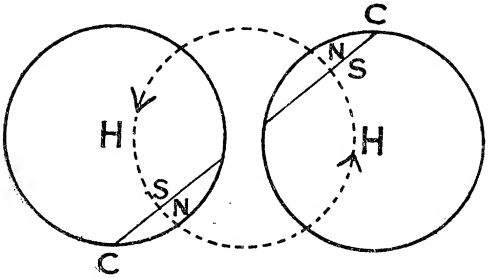

Fig. 4.

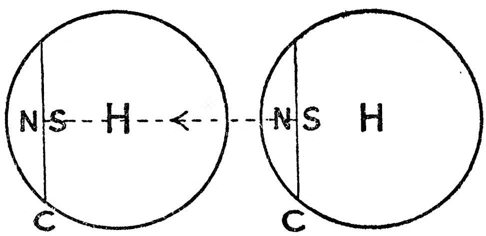

Fig. 5.

metastable position, shown in fig. 5; that the ball should stay in that position at all is due to the friction of the bearings.

If the current through the coil attached to the left-hand ball be clockwise, the ball representing hydrogen, and that through the right-hand coil be anti-clockwise, as representing chlorine (supposed to be a monad, the other affinities being ignored for the moment), then the position taken by the two balls is that shown in fig. 6; it is the only stable position; it is also depicted in fig. 3.

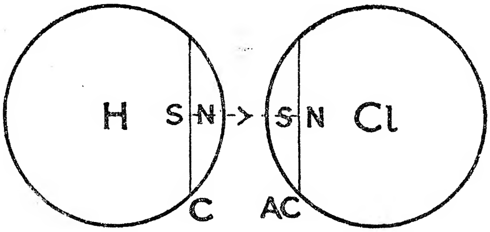

Fig. 6.

In figs. 4, 5, and 6 the dotted lines with arrows indicate the manner in which the lines of either coil thread through the other; and it will be seen that the north pole of one solenoid is always connected with the south pole of the other solenoid.

A figure similar to fig. 4 represents also the position taken when both currents are anti-clockwise; it may be conceived to represent the valency electrons in the molecule Cl_2. There is, of course, also a tendency towards the metastable position shown in fig. 5.

Before passing on to consider the behaviour of dyad atoms, we may regard the halogens; in what respect does chlorine differ from bromine, iodine, and fluorine? If fig. 6 be looked at, it is seen that the diameters of the circular paths of the electrons have been made equal. This is pure guess-work; but if they are equal, and if the velocity of the electron attached to the hydrogen atom is equal to that of the electron attached to the chlorine atom, the periods of rotation of both electrons will also be equal. It may be, however, that the circumference of the circle traversed by the chlorine electron is less or greater than that traversed by the hydrogen electron; and if so, then it is probable that the electrons attached to an atom of fluorine, bromine, and iodine would differ not only from that of chlorine in this respect, but also from each other. The attractive force of a coil depends directly on the amount of electricity which passes through it per second—translated into the language of electrons, on the absolute number of electrons which pass any point of the coil per second. Similarly, the steady or mean part of the

attractive force which a rotating electron can exercise* will depend on the number of times it passes a given point on its orbit per second.

Of two electrons possessing equal linear velocity, that one with the smaller orbit will represent the stronger orbital current, while the attractive force depends on current and area jointly; if they have equal orbits, that one with the greater linear velocity will have the greater attractive force. It would be reasonable to suppose that while the greatest force is exercised by an atom of fluorine the least force or "affinity" is to be ascribed to iodine; and the cause of their difference may be of the nature of that mentioned above.

Taking an atom of oxygen as typical of a dyad atom, it is to be noticed that its two electrons are each moving in an anti-clockwise path relative to the nearest pole, and will therefore repel each other, for they rotate in different hemispheres, and therefore in different directions. Such an atom is shown in fig. 7. They would naturally be assumed to take such a position that their

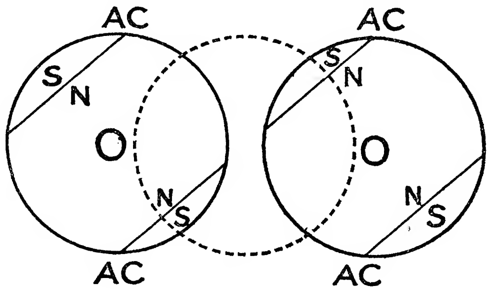

Fig. 7.

planes of rotation would be parallel to and equidistant from the same great circle.

* It must be noted that the present investigation deals only with the magnetic forces of the revolving electrons. Following the method introduced by Gauss into physical astronomy, the charge of each electron may be considered as spread along its orbit so that the quantity on any arc is proportional to the time the electron is in that arc; this representation will give the steady mean forces of affinity, leaving out rapid fluctuations arising from the varying position of the electron. The former include exactly the magnetic forces due to electric currents as here investigated: but there are also other (usually greater) forces due to the static attractions between the charges as thus spread round their orbits. In ordinary galvanic currents the latter forces are compensated by other electrons of the opposite sign revolving in the orbit in the other direction, and an adjustment of similar kind may be understood as introduced here. Or we may note that each negative ring-change must have a compensating positive charge in the nucleus, when the atom as a whole is uncharged, and these two together form a doublet having an electric field roughly of the same general type as the magnetic field of the current, but always of the AC kind; so that the present experimental procedure, employing coils of different numbers of convolutions, is still suitable for general elucidation of the problem.

The molecule of oxygen has the formula O_2; two atoms must lie alongside each other; there is no alternative. There appear from experiment to be two almost equally stable positions: those shown in figs. 7 and 8. The former of these differs little from the hydrogen molecule as shown in fig. 4; it appears, on the whole, to be less stable. Fig. 8 gives the alternative position; it is to be remarked that the proximity to each other of the two north poles makes the resulting lines of force of oval shape.

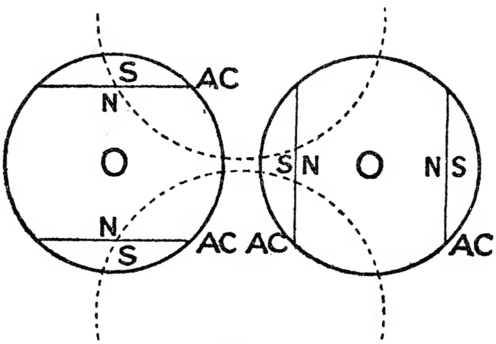

Fig. 8.

Experiments have been made with systems of three balls, which may be conceived to represent O_3, ozone; the electrons are supposed to revolve clockwise. These may occupy two positions; they may form a straight line, or they may be arranged as an equilateral triangle. Both were tried.

The more stable form of an arrangement in line is shown in fig. 9. The position reminds one of that of two hydrogen atoms, combined to form a

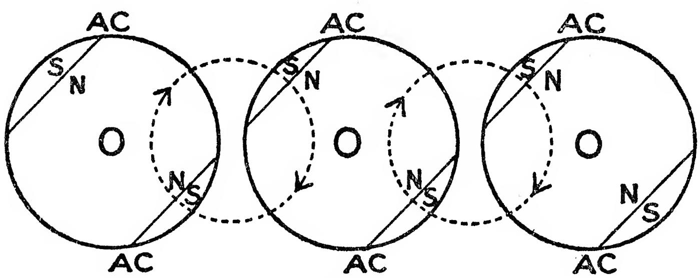

Fig. 9.

molecule, as in fig. 4. A less stable form is that given in fig. 10. Both these exhibit all the electrons rotating in an anti-clockwise direction.

Fig. 10 may be compared with fig. 8; the planes of the electrons are similar.

It is usual for chemists to picture a molecule of ozone as a closed

system; in this case the atoms of oxygen are apparently all dyads. If they are arranged in a row or chain, then the middle atom of oxygen must act as

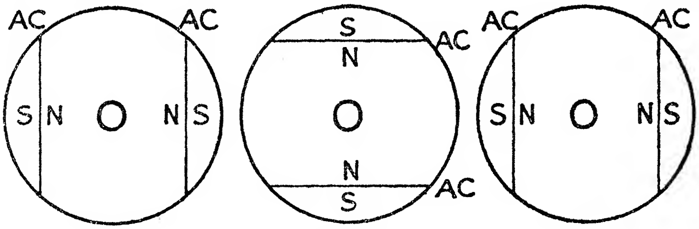

Fig. 10.

a tetrad; in fact, the compound might be termed an "oxide of oxygen." But this idea does not apply to the figure shown; inasmuch as each atom of oxygen carries only two electrons, all atoms are represented as dyad; no experiment has been made with a tetrad atom.

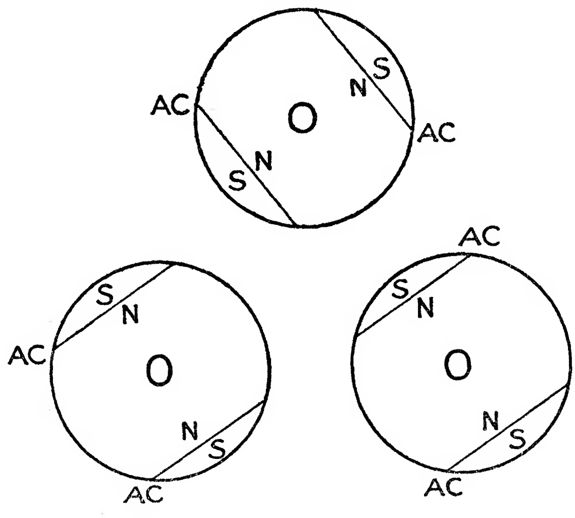

Fig. 11.

A model has been constructed, however, which reveals the configuration taken by three atoms of oxygen placed at the apices of an equilateral triangle. As before, all paths of rotation of the electrons are taken as anti-clockwise. The position of two of the atoms is similar to that assumed in fig. 7 by two atoms of oxygen; that of the electron-path in the third atom is approximately at right angles to those of the other two. It is obvious that not much disturbance would be caused by the disruption of the molecule and the formation of three molecules of oxygen from two of ozone.

The next molecule to be considered was the water molecule. The two

atoms of hydrogen, with the clockwise direction of their electrons, place themselves in juxtaposition to the anti-clockwise electrons of the oxygen atom, with this result: the configuration is a stable one and difficult to disturb. With the conventional configuration H—O—H, the position of the atoms is given in fig. 12.

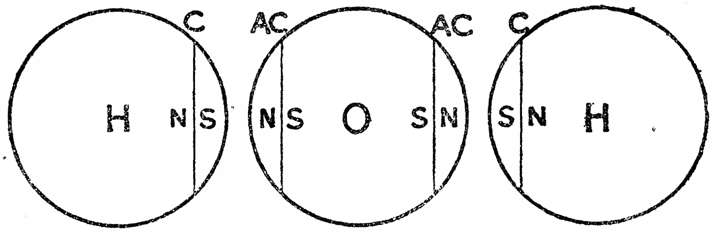

Fig. 12.

Removing an atom of hydrogen, so as to leave O—H, gives the structure shown in fig. 13.

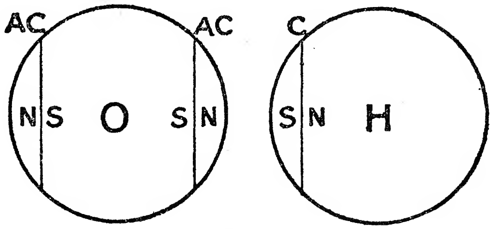

Fig. 13.

It is convenient to add here the usual formula for chlorine monoxide, Cl—O—Cl; it is shown in fig. 14; there are two alternatives, of which the

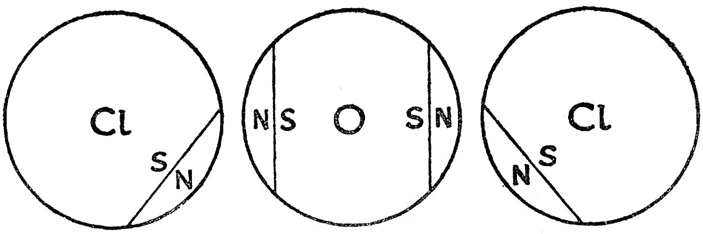

Fig. 14A.

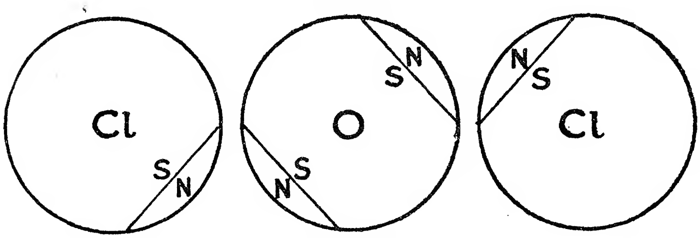

Fig. 14B.

former appears to be the more stable. Hydrogen hypochlorite, H—O—Cl, on the same plan, gives the arrangement shown in fig. 15.

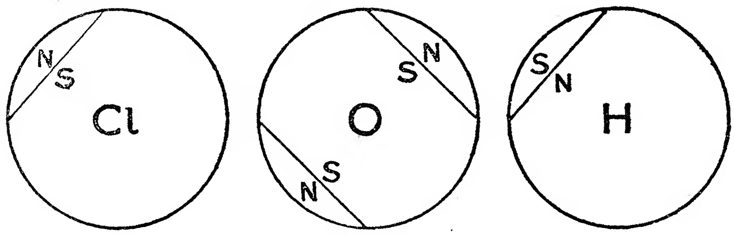

Fig. 15.

Hydrogen hypochlorite and chlorine monoxide, arranged with the atoms at the apices of an equilateral triangle, give the form shown in fig. 16.

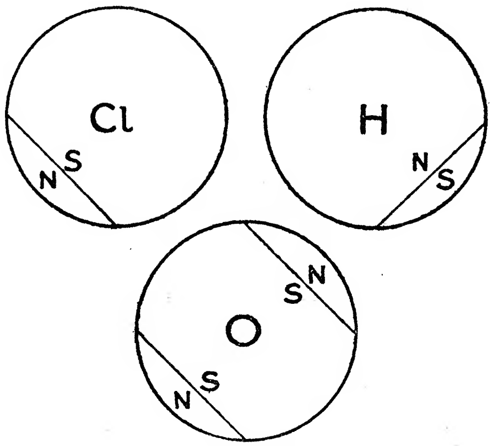

Fig. 16.

These have in some measure analogy with "triangular" ozone, or hydrogen dioxide.

Attempts with four balls did not succeed well; the forces are not sufficient to adjust equilibria against the friction of the needle, except in one or two special cases. Thus, an atom of nitrogen situated at the centre of an equilateral triangle, the corners of which are occupied by three hydrogen atoms, takes up a stable configuration, similar in its way to that of the oxygen and hydrogen atoms in "linear" water. The hydrogen electrons all lie parallel each to a corresponding nitrogen electron. The result is shown in fig. 17.

In conclusion I wish to point out that this is an experimental research. Having postulated a certain structure for some simple atoms, an attempt has been made to ascertain in what manner the atoms would arrange themselves

relatively to each other in the molecule. It is hardly necessary to insist that two-dimensional schemes cannot do more than feebly illuminate the structure

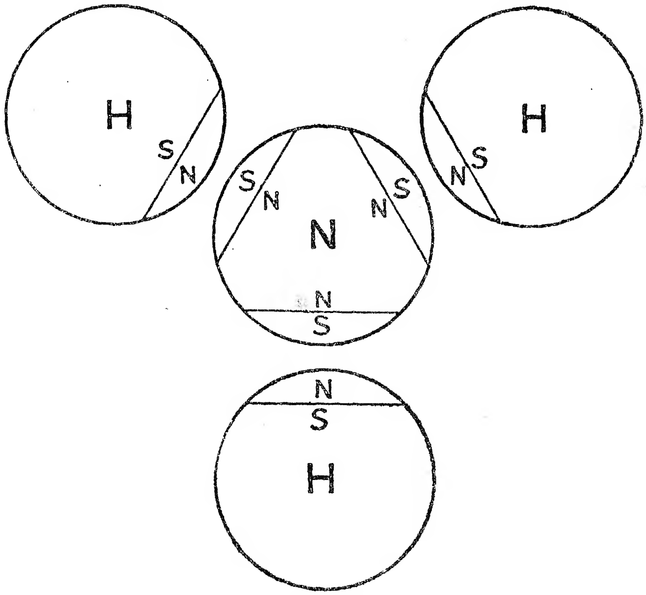

Fig. 17.

of molecules existing in three dimensions; again, that the necessity in mechanical models of preventing the lateral motion of the atoms, and so of adjusting by wires or otherwise the spatial relations between them, removes the actual configurations taken up by such models still further from actuality. Still, all progress in our knowledge of molecular structure has been made by first simplifying the problems to be solved. A scheme in three dimensions, to be manageable, must be on broad simple lines; whether simplification in this case has been carried so far as to destroy all real analogy between such models and molecular structures which may actually exist in nature, time alone can show.

I have to express my warm thanks to Prof. Worthington and to Sir Joseph Larmor for useful criticism.